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(FILE 'HOME' ENTERED AT 07:31:57 ON 19 JUN 2003)

FILE 'CA' ENTERED AT 07:32:11 ON 19 JUN 2003

L1 12752 S (MASS OR SPECIE) (2A) BALANCE
L2 910 S L1 AND ISOTOP?
L3 56 S L2 AND (CR OR CHROMIUM OR CHROMATE)
L4 7 S L3 AND (REDOX OR OXIDAT? OR OXIDIZ? OR REDUC?)
L5 108 S L1 AND ISOTOP? (6A) (DILUT? OR LABEL? OR TRACER OR STANDARD)
L6 110 S L4-5
L7 64 S L6 NOT PY>1997
L8 0 S L6 NOT L7 AND PATENT/DT

=> d l7 bib,ab 1-64

L7 ANSWER 30 OF 64 CA COPYRIGHT 2003 ACS

AN 120:163174 CA

TI C-H Bond Activation by Metal Oxo Species: **Oxidation** of Cyclohexane by Chromyl Chloride

AU Cook, Gerald K.; Mayer, James M.

CS Department of Chemistry, University of Washington, Seattle, WA, 98195, USA

SO Journal of the American Chemical Society (1994), 116(5), 1855-68

AB Chromyl chloride (CrO_2Cl_2) reacts with cyclohexane solvent at 75 °C to give a dark ppt. along with chlorocyclohexane and a small amt. of cyclohexene (in 10.0 and ca. 0.3% yields based on **chromium**). Hydrolysis of the ppt., or treatment with a coordinating org. solvent such as acetonitrile, yields cyclohexanone (8.0%) and chlorocyclohexanone (2.5%). Spectroscopic studies of the ppt. indicate that the ketone products are present intact as σ -only ligands. Iodometric titrns. of the complex show the av. **chromium oxidn.** state to be 3.41. The obsd. org. products account for only 26% of the **chromium oxidizing** equiv. used in the reaction; the remainder are most likely consumed in the formation of ring-opened products such as adipic acid. The three major org. products grow in concurrently during the course of the reaction and are not substantially **oxidized** further under the reaction conditions. Cyclohexene, however, is readily **oxidized** by CrO_2Cl_2 to give mostly ring-opened products with some 2-chlorocyclohexanone and cyclohexanone. The rate of reaction of CrO_2Cl_2 with cyclohexane, monitored via the optical absorbance of the CrO_2Cl_2 vapor above the soln., is first order in **chromium**. Rates were reproducible with no sign of an induction period. Reaction in the presence of the radical trap CBrCl_3 gave some bromocyclohexane. The data indicate that the reaction proceeds by initial hydrogen atom transfer from cyclohexane to CrO_2Cl_2 . The cyclohexyl radical is rapidly trapped by **oxidizing chromium** species via one of three pathways: (i) chlorine atom abstraction, (ii) formation of a C-O bond, and (iii) transfer of a second hydrogen atom. The **mass balance** of the reaction and results from reactions of cyclohexane- d_{12} are consistent with this mechanism. The ability of CrO_2Cl_2 to abstr. a hydrogen atom from cyclohexane is remarkable, as it is a closed-shell diamagnetic species, not a radical. It is proposed that the hydrogen atom abstracting ability derives from the ability of CrO_2Cl_2 to make a strong O-H bond by accepting a hydrogen atom. The strength of the analogous O-H bond made by permanganate can be calcd. from a thermodyn. cycle to be 80 kcal/mol. Using this value for CrO_2Cl_2 provides both a qual. and a quant. understanding of the hydrogen atom transfer step. The implications of this perspective for transition metal mediated hydrogen atom transfer reactions are discussed.

L7 ANSWER 45 OF 64 CA COPYRIGHT 2003 ACS

AN 110:12791 CA

2

TI Scientific considerations for empirical determination of regional source-receptor relationships

AU Hidy, G. M.

CS Desert Res. Inst., Reno, NV, 89506, USA

SO Atmospheric Environment (1967-1989) (1988), 22(9), 1801-20

AB Investigations required to support the design of a large-scale field expt. to derive empirical relationships between source emissions and receptor conditions are discussed. The applications of the approach is on scales where long-range transport of air pollutants, particularly SO_x and NO_x can take place. The region studied was eastern North America. The studies examd. the exptl. concept using tracer releases to track emissions, the availability of suitable tracer technol., the availability of appropriate empirical source-receptor models, the uncertainties and natural variability influencing the expt., and a formal framework to construct a suitable measurement and interpretative design. An expt. can be devised that uses a combination of inert and chem. reactive tracers to establish source-receptor relations, and simulates atm. behavior of SO₂ and NO_x. **Isotopic S and N tracers** are available as well as inert tracers of perfluorocarbons rarely found in the atm. Two empirical model concepts are available, one using a statistical regression format and the other a differential **mass balance**. Based on theor. calcns. and available measurements uncertainties induced with measurements and atm. fluctuations are estd. to be large, making the projected exptl. results uncertain at the outset. A statistical design structure using objective anal. can be specified from meteorol. experience to improve the capability of dealing with the uncertainties. The results of the studies are discussed to provide a foundation for design of a massive aerometric tracer expt. (MATEX).

L7 ANSWER 52 OF 64 CA COPYRIGHT 2003 ACS

AN 106:216709 CA

TI Use of stable sulfur isotopes to monitor directly the behavior of sulfur in coal during thermal desulfurization

AU Liu, C. L.; Hackley, K. C.; Coleman, D. D.

CS Illinois State Geol. Surv., Champaign, IL, 61820, USA

SO Fuel (1987), 66(5), 683-7

AB A method was developed by using stable S isotope analyses to monitor the behavior of S forms in a coal during thermal desulfurization. In this method, the natural stable isotopic compn. of the pyritic and org. S in coal is used as a tracer to follow their mobility during the desulfurization process. This tracer method is based on the fact that the isotopic compns. of pyritic and org. S are significantly different in some coals. Isotopic results of pyrolysis expts. at 350-750° indicate that the S released with the volatiles is predominantly org. S. The pyritic S is evolved in significant quantities only when pyrolysis temps. are >500°. The presence of pyrite has no effect on the amt. of org. S evolved during pyrolysis. The chem. and isotopic **mass balances** achieved from 3 different samples of the Herrin (No. 6) coal of the Illinois Basin demonstrate that this stable **isotope tracer** method is quant. The main disadvantage of this tracing technique is that not all coals contain isotopically distinct org. and pyritic S.

L7 ANSWER 60 OF 64 CA COPYRIGHT 2003 ACS

AN 93:83040 CA

TI On-line data evaluation used in automatic mass spectrometric **isotope dilution** analysis of nuclear fuels

AU Koch, Lothar; Brandalise, Bruno

CS Jt. Res. Cent., Karlsruhe Establ. Eur. Inst. Transuranium Elem., Karlsruhe, D-7500, Fed. Rep. Ger.

SO Annali di Chimica (Rome, Italy) (1977), 67(9-12), 767-72
AB Automatic on-line data evaluation was used for isotope anal. of nuclear fuels. Various automates, (**balance**, α - and **mass**-spectrometers), are linked via special interfaces and 3 minicomputers to an IBM 370. The system described speeds up the analyses and guarantees the confidentiality and data security required for nuclear materials safeguards.

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STN INTERNATIONAL LOGOFF AT 07:41:02 ON 19 JUN 2003

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(FILE 'HOME' ENTERED AT 08:20:20 ON 19 JUN 2003)

FILE 'CA' ENTERED AT 08:20:29 ON 19 JUN 2003

L1 142409 S (SPECIE OR ION OR ANION OR CATION OR CHROMIUM OR NICKEL) (8A) (CONVER? OR INTERCONVER? OR CROSSOVER OR CROSS OVER OR REDOX OR REDUCTION OR REDUCING OR OXIDAT? OR OXIDIZ?)
L2 16826 S L1(6A) (DETECT? OR MONITOR? OR MEASUR? OR DETERMIN? OR FOLLOW? OR ASSAY? OR ANALY? OR ASSES? OR ESTIMAT? OR EVALUAT? OR INVESTIGAT? OR EXAMIN? OR STUDY? OR STUDIE#)
L3 346 S L2 AND ISOTOP?
L4 12 S L2 AND ISOTOP?(2A) (2 OR 3 OR 4 OR TWO OR THREE OR FOUR OR DOUBLE OR TRIPLE OR MULTI OR MULTIPLE OR MULTIISOTOP? OR PLURAL?)
L5 44 S L3 AND (SPIKE OR ADDITION)
L6 37 S L3 AND(CHROMIUM OR 50CR? OR 53CR? OR CR III OR CR VI OR CR###(2A) STATE)
L7 80 S L4-6
L8 52 S L7 NOT PY>1997
L9 28 S L7 NOT L8
L10 9 S L9 AND(DILUT? OR CHROMATOG?)
L11 17173 S (SPECIE OR ION OR ANION OR CATION OR CHROMIUM OR NICKEL) (8A) TRANSFORM?
L12 2930 S L11(6A) (DETECT? OR MONITOR? OR MEASUR? OR DETERMIN? OR FOLLOW? OR ASSAY? OR ANALY? OR ASSES? OR ESTIMAT? OR EVALUAT? OR INVESTIGAT? OR EXAMIN? OR STUDY? OR STUDIE#)
L13 2864 S L12 NOT L2
L14 153 S L13 AND ISOTOP?
L15 11 S L13 AND ISOTOP?(2A) (2 OR 3 OR 4 OR TWO OR THREE OR FOUR OR DOUBLE OR TRIPLE OR MULTI OR MULTIPLE OR MULTIISOTOP? OR PLURAL?)
L16 13 S L14 AND (SPIKE OR ADDITION)
L17 10 S L14 AND(CHROMIUM OR 50CR? OR 53CR? OR CR III OR CR VI OR CR###(2A) STATE)
L18 18 S L15-17 NOT PY>1997
L19 14 S L15-17 NOT L18
L20 2 S L19 AND DILUT?
L21 81 S L8,L10,L18,L20

=> d bib,ab 1-81

L21 ANSWER 62 OF 81 CA COPYRIGHT 2003 ACS

AN 101:3352 CA

TI A least-squares approach to the quantitation of stable isotopes in mass spectrometry

AU Lee, Wai Nang Paul; Whiting, James S.; Fymat, Alain L.; Boettger, Heinz G.
CS Dep. Pediatr., Univ. California, Los Angeles, CA, 90024, USA

SO Biomedical Mass Spectrometry (1983), 10(12), 641-5

AB A least-squares method was adapted for the quantitation of stable isotopes in mass spectrometry. The method uses the normalized spectra of the 2

isotope species and the obsd. intensities to calc. the isotope ratio by a series of matrix manipulations and is applicable to systems with multiple overlapping ions. The method is used to establish the expected sensitivity of measurement of ^{15}N enrichment of an amino acid by a focal plane mass spectrometer equipped with an electrooptical ion detector. Since multiple spectral peaks are used, the relation between addnl. spectral information and the redn. in variance in ion-current statistics can be demonstrated. The example suggests a method for optimization of simultaneous ion monitoring or limited scanning methods by **monitoring** the no. of **ions** which would contribute to the **redn.** of variance of the ion current of the compd. of interest.

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STN INTERNATIONAL LOGOFF AT 08:51:17 ON 19 JUN 2003